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Mathys & Squire**(54) Heterophasic ceramic composition**

(57) A heterophasic ceramic composition comprises a major amount of barium titanate and a minor amount of a lead germanate composition having the formula



wherein $1 < x \leq 6$, y ranges from 1 to 3, and z ranges from more than 0.0 to 0.75 y , the ceramic composition being characterized in that densification is effected by liquid phase sintering to yield the heterophasic structures in which the lead germanate composition provides a continuous intergranular phase which separates the barium titanate phase into discrete localized volumes.

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FIG. 1

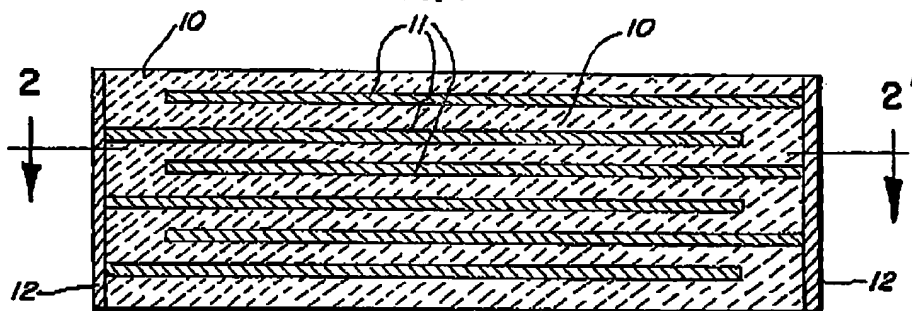
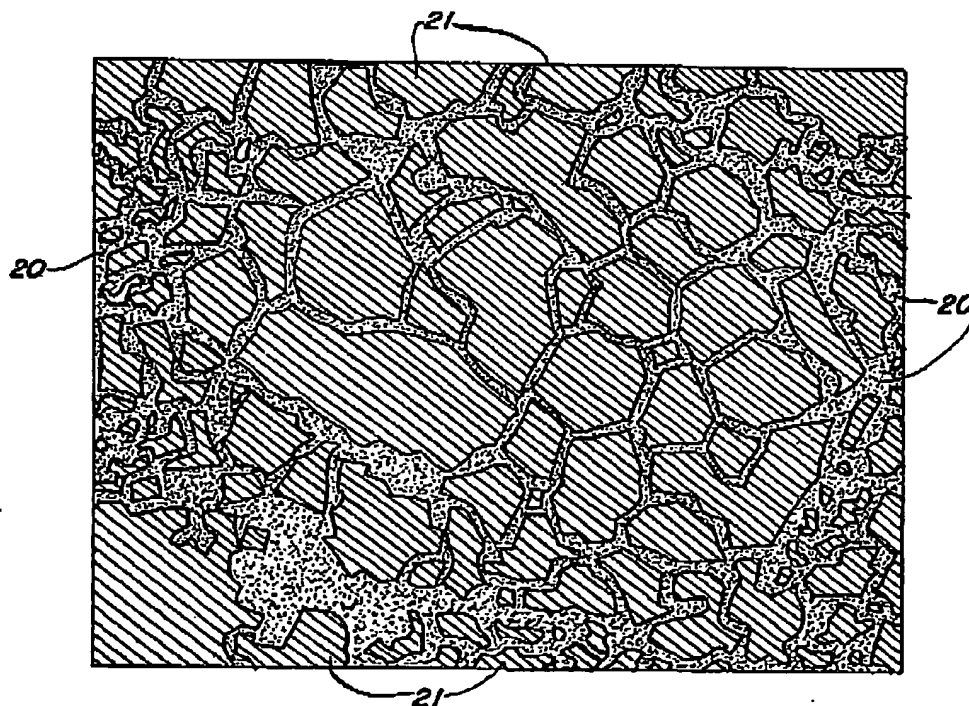


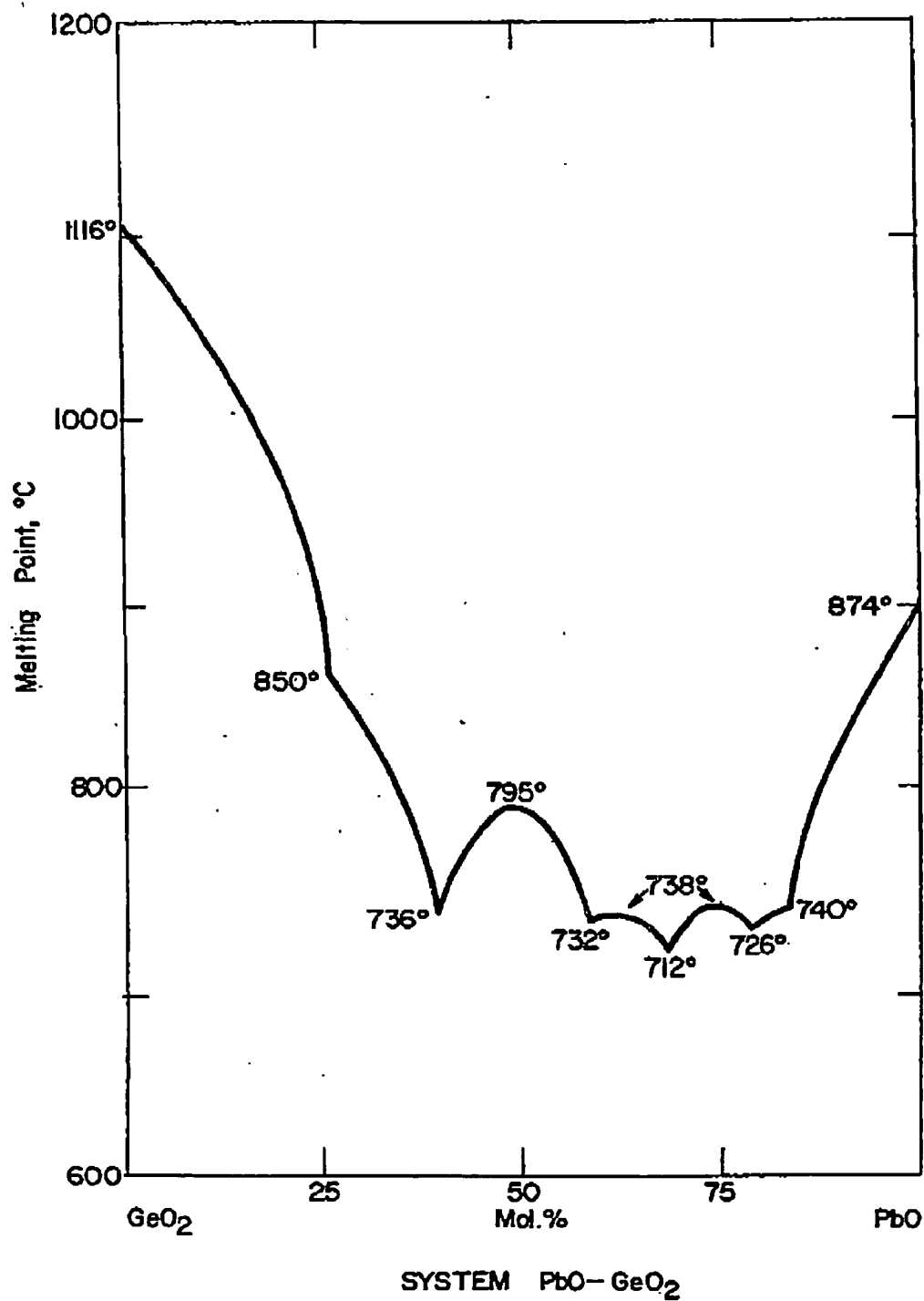
FIG. 2



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FIG. 3



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SPECIFICATION

Heterophasic ceramic composition

This invention relates to novel ceramic compositions, to methods for producing them and to ceramic capacitors utilizing such compositions.

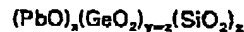
- 5 In modern electronic circuitry where high volumetric efficiency in capacitance is required, miniaturized capacitors based upon high dielectric constant materials are increasingly important. Most representative of all high dielectric ceramics is barium titanate, a material that offers a wide range of applications in the fabrication of monolithic multi-layer ceramic capacitors. Such multi-layer capacitors are well known in the art and comprise alternate layers of a ceramic dielectric and metal electrodes, bonded together in a monolithic structure. Alternate electrodes are connected together at one end of the structure and the other electrodes are connected together at the other end. Usually, the electrodes are connected together by a metal terminal applied to the ends of the structure. In the firing of such structures based upon conventional barium titanate ceramics, temperatures of the order of 1300—1400°C are required, and at these high temperatures in air expensive electrode systems utilizing the noble metals such as platinum and palladium must be used.

Our copending U K Patent Application No. 41933/78 Serial No. 2014126 describes and claims a BaTiO₃ ceramic composition that can be fired at relatively low temperatures and provide, by liquid sintering, a heterophasic composition of high dielectric strength and low dissipation factor.

- 20 According to said application, there are provided compositions comprising a major amount of BaTiO₃ and from 1 to 33 volume percent of Pb₃Ge₃O₁₁, said composition being capable of forming a heterophasic ceramic body by liquid phase sintering at a temperature within the range of about 750°—1050°C.

The present applications provided further compositions of similar utility.

- 25 According to the present invention there are provided heterophasic ceramic compositions comprising a heterophasic ceramic composition comprising a major amount of barium titanate and a minor amount of a lead germanate composition having the formula



- 30 wherein $1 < x \leq 6$, y ranges from 1 to 3, and z ranges from 0.0 to 0.75 y , the ceramic composition being characterized in that densification is effected by liquid phase sintering to yield the heterophasic structure in which the lead germanate composition provides a continuous intergranular phase which separates the barium titanate phase into discrete localized volumes, with the proviso that when said heterophasic ceramic composition comprises from 1 to 33 volume percent of said lead germanate composition and x is 5 and y is 3, z is other than zero.

- 35 Compositions according to the invention can be fired at 750—1050°C to provide heterophasic ceramic bodies of high dielectric strength and low dissipation factor. The relatively low firing temperature permits use of inexpensive, non-noble metals and alloys thereof as electrodes in the fabrication of monolithic multi-layer capacitors.

The invention will now be described in more detail with particular reference to the accompanying drawings of which:

- 40 Figure 1 is a cross-sectional view of the monolithic multi-layer capacitor of this invention having alternate layers of ceramic dielectric 10, staggered electrodes 11, and terminal contact electrodes 12 at each end.

- Figure 2 is a sectional view of the ceramic dielectric of Figure 1 taken along the axis 2—2'. Illustrated in the heterophasic microstructure of the mature ceramic comprising a continuous lead germanate derived phase 20 and a discrete barium titanate phase 21.

Figure 3 is a phase diagram of the PbO—GeO₂ system showing the melting points of various lead germanate compositions.

- For the practice of this invention, the system barium titanate—lead germanate was found to be particularly suitable. For example, BaTiO₃ of from about 1 to about 10 micron particle size is admixed with from about 1 to about 33, preferably from about 5 to about 25, volume % of a lead germanate composition; minor amounts of other ceramic materials can be incorporated in the mixture, for example, up to about 25 volume % of one or more of the following: SrTiO₃, CaZrO₃, TiO₂, and the like. After the ceramic body is formed, a metal electrode of silver, copper, aluminum, iron, cobalt, nickel, or mixtures thereof is deposited thereon and multiple layers of the combination are stacked and pressed into a monolithic capacitor structure. The green ceramic structure is then fired, usually in air, for generally from about 1 to about 60, typically from about 2 to about 45, and preferably from about 2 to about 20 minutes, at a temperature of generally from about 750 to about 1050, typically from about 800 to about 1000, and preferably from about 850 to about 950°C. If firing temperatures substantially in excess of about 1050°C were used, relatively inexpensive, non-noble metals and alloys thereof could not be used in the fabrication of monolithic multi-layer capacitors. Temperatures substantially below about 750°C are either not effective or require excessively long firing times.

Although firing temperatures and time for firing are interrelated (i.e., the higher the firing

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temperature, the shorter the firing time, and vice versa), it has been found that firing times in excess of about 60 minutes are unnecessary and uneconomical. Firing times substantially less than about 1 minute are not effective to produce the desired result even at relatively high firing temperatures.

- 5 Firing of the ceramic structure can also be carried out in controlled atmospheres, for example in an atmosphere having a low partial pressure of oxygen. Consolidation, or densification, of the ceramic occurs by liquid phase sintering to yield a pore-free, heterophasic structure in which a continuous intergranular lead germanate derived phase separates the major barium titanate phase into discrete localized volumes. Under the above-described conditions, there is essentially no reaction between the barium titanate phase and the lead germanate derived phase.
- 10 In the barium titanate-lead germanate system it was found that the degree of densification increased with the amount of liquid phase present. Dielectric constant, however, decreased with increasing amounts of liquid phase. By considering both dielectric and densification characteristics, the preferred amount of liquid phase for rapid sintering at 1000°C was found to be from about 10 to about 15 volume %, which provided a ceramic having dielectric constant values in the range of from about 1000 to about 1500.

15 The term "lead germanate" in this specification is meant to include lead and germanium containing compounds such as $Pb_5Ge_3O_{11}$, and lead, germanium, and silicon containing compounds as defined by the formula:



- 20 where $1 < x \leq 6$, y ranges from 1 to 3, and z ranges from 0.0 to 0.75 y . Mixtures of two or more compounds can also be used.

- Lead germanate compositions suitable for the liquid phase sintering step can be prepared by heating various mixtures of PbO and GeO_2 up to temperatures of about 1000°C. The phase diagram in Figure 3 shows the melting points for various molar ratios of PbO and GeO_2 . For the purposes of this invention, lead germanate compositions having melting points below about 850°C are preferred. Because of the relatively high cost of GeO_2 , a portion of it can be replaced advantageously with SiO_2 .

- The lead germanate composition having the formula $Pb_5Ge_3O_{11}$, is a preferred composition because it melts congruently (i.e., solid and liquid phases have identical compositions) to provide a low viscosity melt which is advantageous for rapid and complete liquid phase sintering. The composition is prepared by heating in a platinum crucible at about 750°C 5 moles of PbO and 3 moles of GeO_2 until a clear liquid is formed. The cooled product, having the formula $Pb_5Ge_3O_{11}$, is crushed and powdered in a mortar and pestle, screened through a 325 mesh sieve, and further reduced by ball milling. The final powder has a particle size ranging from about 0.5 to about 50 microns with the greatest concentration at about 5 microns.

- 35 The following description and data are presented to illustrate the practice and advantages of the instant invention. The materials used were reagent grade PbO and GeO_2 , and research grade $BaTiO_3$. The lead germanate composition was prepared as described above. The research grade $BaTiO_3$ had an average particle size of about 1 micron.

- For the purpose of measuring electrical properties, $BaTiO_3$ was admixed with 10, 20, and 30 volume % of $Pb_5Ge_3O_{11}$. Pellets 1.25 cm in diameter and 0.2 cm thick were prepared in a die by dry pressing at a pressure of 30,000 psi. The pellets were sintered isothermally at 850, 900, 950, 1000, and 1050°C for 5 minutes. Quick air-drying silver paste was used to provide electrodes on the surface of the specimens.

- Capacitance and dissipation factor were measured over a temperature range of 25 to 160°C. Ratings were recorded at 100 KHz. The weak field signal voltage applied across the specimens was 0.5 volts r.m.s.

- Table I lists dielectric constants, K' , and dissipation factors, $\tan \delta$, for $BaTiO_3$ — $Pb_5Ge_3O_{11}$ ceramic compositions containing 10, 20, and 30 volume % of $Pb_5Ge_3O_{11}$ sintered at 950°C. These data illustrate that low temperature sintering of the compositions of this invention provides ceramic capacitors possessing excellent electrical characteristics.

TABLE I
Dielectric Measurements on Liquid Phase Sintered

$\text{BaTiO}_3(1 \text{ micron}) + \text{Pb}_5\text{Ge}_3\text{O}_{11} (X)$

$T_s = 950^\circ\text{C}$, $t_s = 5 \text{ min.}$ 100 KHz

T(°C)	X = 10 Vol. %		X = 20 Vol. %		X = 30 Vol. %	
	K'	tan δ	K'	tan δ	K'	tan δ
25	1210	0.012	825	0.016	490	0.016
60	1180	0.010	822	0.017	495	0.015
70	1176	0.009	—	—	—	—
80	1205	0.009	828	0.013	498	0.0156
90	1248	0.009	841	0.014	—	—
100	1302	0.009	885	0.012	516	0.016
110	1357	0.0096	950	0.014	526	0.016
120	1440	0.0095	954	0.012	544	0.018
130	1319	0.009	911	0.011	537	0.016
140	1193	0.010	844	0.013	514	0.015
160	1000	0.012	—	—	467	0.020

Table II lists dielectric constant and dissipation factor measurements for a BaTiO_3 —10 Vol.% $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ composition sintered at temperatures in the range of 850—1050°C. These data illustrate that especially good electrical characteristics are obtained with sintering temperatures at the high end of the range 850—1050°C. Satisfactory electrical properties, however, are obtained over the entire range of sintering temperatures.

Table III lists comparative data for ceramic compositions liquid phase sintered at 900°C for 20 minutes with PbGeO_3 derived from $(\text{PbO})(\text{GeO}_2)$; $\text{Pb}_5\text{Ge}_3\text{O}_{11}$ derived from $(\text{PbO})_5(\text{GeO}_2)_3$; $\text{Pb}_5\text{Ge}_2\text{SiO}_{11}$ derived from $(\text{PbO})_5(\text{GeO}_2)_2\text{SiO}_2$; and $\text{Pb}_5\text{GeSi}_2\text{O}_{11}$ derived from $(\text{PbO})_5(\text{GeO}_2)(\text{SiO}_2)_2$.

The data illustrate that ceramic compositions with excellent electrical properties can be obtained by liquid phase sintering with various lead germanate compositions and various lead germanate-silicate compositions.

Although this invention has been disclosed with particular reference to certain preferred embodiments thereof, it is understood that variations and modifications can be effected within the spirit and scope of the appended claims. It is intended that all matter contained in the above description and tables or shown in the accompanying drawings shall be interpreted in an illustrative and not in a limiting sense.

TABLE II
Dielectric Measurements on Liquid Phase Sintered
 BaTiO_3 (1 micron) + 10 Vol. % $\text{Pb}_3\text{Ge}_3\text{O}_{11}$
 $t_s = 5 \text{ min.}$

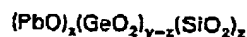
T (°C)	$T_s = 850^\circ\text{C}$		$T_s = 900^\circ\text{C}$		$T_s = 950^\circ\text{C}$		$T_s = 1000^\circ\text{C}$		$T_s = 1050^\circ\text{C}$	
	K'	$\tan \delta$	K'	$\tan \delta$	K'	$\tan \delta$	K'	$\tan \delta$	K'	$\tan \delta$
25	868	0.0125	963	0.012	1210	0.012	1315	0.021	1430	0.024
60	840	0.0085	945	0.009	1180	0.010	1310	0.018	1428	0.0175
70	858	0.009	—	—	1176	0.009	1300	0.016	—	—
80	867	0.010	—	—	1205	0.009	—	—	1425	0.015
90	875	0.011	986	0.01	1248	0.009	—	—	1478	0.014
100	881	0.011	1031	0.0103	1302	0.009	1367	0.014	1575	0.015
110	940	0.012	1114	0.0120	1387	0.0086	1475	0.014	1775	0.015
120	963	0.0135	1157	0.0135	1440	0.0095	1568	0.015	1830	0.0143
130	930	0.016	1075	0.016	1318	0.009	1480	0.016	1682	0.013
140	858	0.018	983	0.015	1193	0.010	1350	0.013	1500	0.013
160	738	0.023	837	0.017	1000	0.012	1130	0.018	1240	0.013

TABLE III
Dielectric Measurements on Liquid Phase Sintered BaTiO₃

T(°C)	T _S = 900°C.			t _S = 20 min.				
	BaTiO ₃ + 10 Wt. % PbGeO ₄		BaTiO ₃ + 10 Wt. % Pt ₃ Ge ₂ O ₁₁		BaTiO ₃ + 10 Wt. % Pb ₂ Ge ₃ SiO ₁₁		BaTiO ₃ + 10 Wt. % Pb ₂ GeSi ₂ O ₁₁	
	K'	tan δ	K'	tan δ	K'	tan δ	K'	tan δ
25	1068	1.8	1075	2.0	903	1.7	907	1.6
40	—	—	1092	1.9	910	1.6	904	1.3
60	1075	1.7	1124	2.1	924	1.8	928	1.3
80	1080	1.4	1187	2.3	954	1.7	950	1.3
100	1135	1.4	1215	2.2	1034	1.7	1015	1.4
120	1312	1.4	1422	2.1	1105	1.4	1095	1.3
140	1150	1.2	1300	2.3	1087	1.5	1092	1.2
160	—	—	1085	2.3	978	1.8	920	1.4

CLAIMS

1. A heterophasic ceramic composition comprising a major amount of barium titanate and a minor amount of a lead germanate composition having the formula



- 5 where $1 < x \leq 6$, y ranges from 1 to 3, and z ranges from 0.0 to 0.75 y , the ceramic composition being characterized in that densification is effected by liquid phase sintering to yield the heterophasic structure in which the lead germanate composition provides a continuous intergranular phase which separates the barium titanate phase into discrete localized volumes, with the proviso that when said heterophasic ceramic composition comprises from 1 to 33 volume percent of said lead germanate composition and x is 5 and y is 3, z is other than zero. 5
- 10 2. A composition according to Claim 1 comprising a major amount of barium titanate and from about 1 to about 33 volume % of the lead germanate composition, wherein the liquid phase sintering is effected at a temperature in the range of from about 750 to about 1050°C. 10
- 15 3. A composition according to Claim 1 and substantially as hereinbefore described. 15
4. A high dielectric constant ceramic capacitor comprising a heterophasic dielectric ceramic body formed of a heterophasic ceramic body formed of a heterophasic ceramic composition as claimed in any preceding claim and electrode metal. 15

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